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(54) (57) Process for preparation of polythiiranes by propylene sulfide polymerization or copolymerization thereof with ethylene sulfide and allylthioglycidyl ether in hydrocarbon solvent media, in the presence as catalyst of a cadmium-bis-allylmercaptide under stirring a reaction mass, characterized in that to improve the physico-mechanical properties of polymers and vulcanizates thereof, the stirring is carried out by coaxial cylinders with a mixture shear flow.

The invention relates to production processes of polythiiranes and can be used in the chemical industry and polymer vulcanizates having high oil resistance and low gas permeability – for the manufacture of hoses and tanks for oil products, gaskets, etc.

Known in the art is a process for preparing polythiiranes in the polymerization of propylene sulfide or its copolymerization with ethylene sulfide and allylthioglycidyl ether in a hydrocarbon solvent medium, in the presence of, as catalyst, a cadmium-bis-allylmercaptide

under stirring a reaction mass. According to this process, the catalyst and a monomer mixture are dumped in a conventional cylindrical reactor, using a shaking device for carrying out a stirring step therein /1/.

A disadvantage of this process resides in the impossibility to continuously trace polymerization reaction. Periodic sampling by a viscosimeter built-in a reactor provides delayed information, which is coupled with an inadequate reproducibility of operations, with the result that the obtainable product has a low degree of crystallinity and the unsatisfactory physico-mechanical properties of polymers and vulcanizates thereof.

An object of the invention is to improve the physico-mechanical properties of polymers and vulcanizates thereof.

Said object is achieved owing to the fact that according to a process for producing polythiiranes by propylene-sulfide polymerization or its copolymerization with ethylene sulfide and allylthioglycidyl ether in a hydrocarbon solvent medium, in the presence of, as catalyst, a cadmium-bis-allylmercaptide under stirring a reaction mass; a stirring operation is carried out by coaxial cylinders with a mixture shear flow.

Essence of a process consists in the following.

A stationary reactor is mounted from two coaxial cylinders on a common bottom. The containing structure thus formed is loaded with a reaction mixture, followed by a third rotary coaxial cylinder immersed in a narrow space annulus between two fixed cylinders. The distance between the lower side of the rotary cylinder and the bottom is several mm. The third coaxial cylinder is brought to rotation by an electric motor with a hollow axle owing to which the linear dependence of a force twisting moment is maintained from a voltage applied to the motor control winding. A shear stress is determined by the twisting moment of the electric motor and the geometric dimensions of a circular working unit wherein polymerization reaction is carried out. The twisting moment is pre-set by the supply voltage of the motor. A period of rotation of a rotor which is the third coaxial cylinder immersed in the space annulus

between the two fixed cylinders is measured by a photodiode period-of-rotation pulse transmitter. Recording of pulses in the digital form is carried out by a frequency meter and a transcriptor with an electrically controlled digital printing machine. Flow shear velocities as measured, enable one to describe polymerization macrokinetics.

Experiments are made at 20-50°C (preferably at 30°C) and at atmospheric pressure. The initial voltage at the terminals of an electric motor is 2 V. Upon dumping monomers in a mass (or in a solvent) and a catalyst in a reactor, the latter is controlled thermostatically, and an operation is carried out under constant conditions.

Example 1. Propylene sulfide polymerization (PS) under the action of cadmium-bis-allylmercaptide (CBAM) in a hydrocarbon solvent medium-toluene.

PS 14.8° g ~ 15 ml

Toluene 85 ml

Load (total 100 ml solution)

PS concentration in toluene is 2 mol/l

CBAM concentration is 1% by weight, as calculated for PS (0.148 g CBAM is taken for 100 ml of solution). A 150 ml reactor is loaded with a 50 ml reaction solution. The temperature in an ultra airswitch - 30°C. Electric motor supply voltage – 2 V. The time of one revolution of a reactor rotor – no-load stroke – 0.349 s. Dynamic toluene viscosity – 0.457 poise at 30°C.

The Table shows data on the dependency of reaction mixture viscosity at 30°C on reaction time.

Time, min	Dynamic viscosity, Poise	Intrinsic viscosity, dl/g	Medium viscosity molecular mass $M_p \cdot 10^{-3}$
15	0,38	0,075	10
35	0,49	0,104	10,2
55	0,87	0,212	25
75	1,34	0,315	40

95	1,75	0,40	55
115	2,07	0,45	63
135	2,33	-	-
155	2,40	0,56	80
175	2,40	0,56	80
195	2,39	-	-
215	2,30	0,53	75
255	2,30	0,53	75

- - M_{η} – polypropylene sulfide (PPS) medium viscosity molecular masses, as calculated by Eskin equation $[\eta] = 0.33 \cdot 10^{-4} \cdot M^{0.86}$ (benzene, 20°C).

A PPS synthesis parallel experiment made in a reactor provided with a magnetic stirrer indicates an almost complete coincidence of the values of molecular mass over a period of 225 min – 68000. The radiograms of PPS samples obtained in a reactor with coaxial cylinders go to show a higher degree of crystallinity vs the PPS samples synthesized in the reactor with the magnetic stirrer.

The differential thermal analysis (DTA) of the sample obtained in a reactor with coaxial cylinders gives one melting endothermic effect at a temperature comprised between 58 and 60°C, while the sample obtained in a reactor with a magnetic stirrer produces a very wide peak at 50°C, a factor that testifies to its lower degree of crystallinity.

Example 2. PS polymerization on PPS “living” chains. A reaction solution, prepared for Example I, is kept for 14 days in the amount of 50 ml, at room temperature in a conic flask with a ground-in cork. A partially polymerized solution is added with a 7.5 ml PS, and 50 ml are loaded from a diluted solution in a reactor with the coaxial cylinders. Temperature is maintained at $30 \pm 0.5^{\circ}\text{C}$. The initial supply voltage of an electric motor – 2 V. Duration of the experiment – 270 min. Initial viscosity – 0.022 poise, final viscosity - 2 poise. The degree of conversion is 93% by weight, i.e. the depth of change is such that chain growth is necessarily controlled by diffusion. In spite of this, likewise in Example I, radiograms and DTA provide indices of the quality of products produced in a coaxial cylinder stirring reactor, which are

higher than in the conventional one.

Example 3. PS polymerization parallel experiment in two reactors:

- a) with coaxial cylinders,
- b) in a test tube provided on a shaking device.

Reaction mixture composition

CBAM 0.148 g

PS 14.8 g

Toluene 85 ml

50 ml of solution are dumped in a coaxial reactor, and the experiment is made for 360 min, at 30°C. The remaining 50 ml are dumped in an airtight test tube and shaken at 30°C on an apparatus for 360 min. The final viscosity of products in both reactors is about 6 poise, albeit radiograms show that the crystallinity of a product produced in a coaxial reactor is higher than the product to be obtained in the test tube.

Example 4. Preparation of ternary vulcanizable elastomer. Monomer characteristics.

Ethylene sulfide (ES) – a mobile colorless fluid having a specific acrid smell. Molecular weight 60, boiling temperature 55 - 56°C, $\alpha_4^{20} = 1.012$, $n_D^{20} = 1.4940$. A chromatogram shows that a basic product constitutes 99.4%. PS – a colorless fluid with an acrid smell. MW 74, boiling temperature 74-76 °C, 755 mm Hg, $\alpha_4^{20} = 0.956$, $n_D^{20} = 1.4753$. A chromatogram shows that a basic product accounts for 99.8%. Allylthioglycid ether (ATGE) – a thick fluid with a pungent smell, produces very aggressive effects on the mucous membranes. MW 130, boiling temperature amounts to 47.5-48 °C/2 mm Hg or 190-195 °C/760 mm Hg, $\alpha_4^{14} = 1.07$, $n_D^{20} = 1.4920$. Solvent – toluene, MW 92, boiling point 110 °C, $\alpha_4^{20} = 0.87$, $n_D^{20} = 1.497$.

CBAM is produced in the following manner.

A cadmium acetate solution in methanol is dropped to allylmercaptan. A precipitate is washed with an ethyl ether and stored in a closed glass vessel in an argon atmosphere, with no exposure to light. CBAM catalyst – a white powder being dissolved during polymerization in

a monomer to form a transparent solution. ES and PS are obtained from respectively ethylene carbonate and propylene carbonate by adding potassium thiocyanate thereto. The synthesized ES and PS are freed of the traces of moisture and carbon dioxide over a zeolite, followed by distillation over a calcium hydride. The potassium thiocyanate is dried at 160 °C. An allylthioglycide ether is synthesized from an allyl alcohol and ethuylchlorohydrin, in the presence of tetravalent tin, a three-membered cycle is closed with alkali, followed by substitution of an oxygen atom with a sulfur atom. During an experiment, a monomeric mixture is prepared, ppm (total 1.00):

PS	0.672
ES	0.266
ATGE	0.062

Said monomer mixture is added with 1% by weight of CBAM, as calculated for the mass of monomer mixture, and also a solvent –toluene whose volume 5-6 times exceeds that of the reaction mixture (or – to be more exact – for each 15 volumes of the latter – 85 volumes of the solvent). The solution is agitated until a catalyst is dissolved completely in a coaxial reactor provided in a thermostat at 30°C. The initial supply voltage of an electric motor is pre-- set 2 V. A record of duration of one revolution of a reactor rotor is switched on. After a period of six hours, during which the intensity of increasing viscosity is recorded without interruption, the operation is terminated, an instrument is switched off and left till the next morning to provide a “matured” product. On the following day, the contents of the reactor are dumped in a containing structure with a tenfold excess of cooled methanol. The methanol – precipitated polymer from the reactor is separated from the solvent and alcohol, dried in vacuo at 25-30 °C and suspended.

Product output 90-93% by weight; viscosity, η , poise:

<u>At 30 °C</u>	<u>40 °C</u>	<u>61.5 °C</u>
741852	146824	29950

MW ~ 70000

A ternary elastomer before vulcanization is analyzed for the contained homopolymers in the following manner: a small product sample is dissolved in benzene and chloroform to find out the presence of a homopolymer of ethylene sulfide which is insoluble in these solvents. If the sample is dissolved completely – no ES homopolymer is available.

To determine the presence of a PS homopolymer, applied is a method of turbidimetric titration. On titration of an elastomer sample, monomodal curves are obtained, which clearly indicates the absence of the PS homopolymer.

Availability of multiple bonds in an elastomer, which are necessary for the final stage – cure is verified by an IR spectrum for an absorption band that might be present (1640 cm^{-1}).

A curing operation is carried out on rollers at $140\text{ }^{\circ}\text{C}$.

The composition of an elastomer pure gum vulcanizate according to Example 4 is as follows (w.p.):

Elastomer	100
Sulfur	0.3
Accelerator component (tetraethylthiuram disulfide)	0.3
zinc oxide (activator)	1
Stearic acid	1
Antioxidant (phenyl-2-naphthyl- amine)	0.2

Vulcanizate, physico-chemical properties

Tensile rupture strength, kgf/cm^2	80-110
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Relative elongation at rupture, %	195-250
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Permanent elongation,% 9.3-12

Swelling in gasoline
in 24 hrs, % 2.8-3

Swelling in oils
-“, % 0.8-2.8

Permeability constant
involving the nitrogen
25 °C, 2 at, cm³/at.cm² . s 1.65-2.35 .10⁻⁹

As can really be seen from the examples, the disclosed process enables one to obtain polymers with higher crystallinity, as compared to prior art, and, consequently, to improve the physico-mechanical properties of polymers and vulcanizates based thereon.

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filed on November 14, 2001
in the name of ESSILOR INTERNATIONAL COMPAGNIE GENERALE
D'OPTIQUE
for : "High index and high impact resistant polythiourethane/urea
material, method of manufacturing same and its use in the optical field"

Dear Sirs,

We refer to your letter of February 24, 2005 concerning the above
mentioned patent application.

Please find enclosed the English translation of the SU 1085991.

Very truly yours.

Alain CATHERINE

Encl